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**(19) AUSTRALIAN PATENT OFFICE**

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**FUEL OIL EMULSIFIERS**

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**Huntsman Surfactants Technology Corporation**

**(54) Inventor(s)**  
**John Kevin Bacon**

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COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1973

APPLICATION FOR A PATENT

563404

I, We HYDROLINE AUSTRALIA PTY. LTD.

of 580 Boundary Road, Coopers Plains, Queensland 4108, Australia

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 21-5-87

hereby apply for the grant of a Patent for an invention  
entitled:

"Emulsions"

which is described in the accompanying Provisional specification.

My, Our address for service is care of GRIFFITH HASSEL & FRAZER,  
Patent Attorneys of 71 York Street, Sydney 2000, in the  
State of New South Wales, Commonwealth of Australia.

Dated this 5th day of December, 1983

HYDROLINE AUSTRALIA PTY. LTD.

By their Patent Attorneys

GRIFFITH HASSEL & FRAZER

TO: THE COMMISSIONER OF PATENTS  
COMMONWEALTH OF AUSTRALIA

LODGED AT SUB-OFFICE  
5 DEC 1983  
Sydney

COMPLETE AFTER PROVISIONAL SPECIFICATION No. 36343/84

ASSIGNEE

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952 (AS AMENDED)

DECLARATION IN SUPPORT OF AN APPLICATION FOR A PATENT

Name of applicant) In support of an Application made by: HYDROLINE AUSTRALIA PTY. LTD.

Title) for a patent for an invention entitled: "Emulsions"

Full name of I, JOHN KEVIN BACON  
Signature) of 27 Jindivick Street, Jindalee 4074, Queensland, Australia  
Address of signature)

do solemnly and sincerely declare as follows:

1. I am authorised by the above mentioned applicant for the patent to make this Declaration on its behalf.

2. The name and address of each actual inventor of the invention is as follows:

Insert details of inventor/s) John Kevin Bacon, of 27 Jindivick Street, Jindalee 4074, Queensland, Australia

Insert details of assignment, etc.) and the fact(s) upon which the applicant is entitled to make this application are as follows:  
applicant is the assignee of the said invention from the said inventor.

3. The basic application(s) as defined by Section 141 of the Act was(were) made as follows:  
Country ..... on .....  
in the name(s) .....  
and in ..... on .....  
in the name(s) .....  
and in ..... on .....  
in the name(s) .....

4. The basic application(s) referred to in the preceding paragraph of this Declaration was(were) the first application(s) made in a Convention country in respect of the invention the subject of this application.

(Place and date of signing) Declared at BRISBANE this 21st day of NOVEMBER 1983.

Signed: J. K. Bacon

Position: MANAGING DIRECTOR

GRIFFITH HASSEL & FRAZER, P.O. BOX 2133, G.P.O., SYDNEY, N.S.W. 2001 AUSTRALIA

(12) AUSTRALIAN PATENT ABRIDGMENT

(19) AU

(11) AU-B-36343/84

(54) FUEL OIL EMULSIFIERS

(71) HYDROLINE AUSTRALIA PTY. LTD.

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(72) JOHN KEVIN BACON

(74) GH

(56) 50625/69 436840 25.1, 86.7, 28.8, 20.6

13518/70

25.1, 86.7, 28.8

GB 2066288

(57) Fuel oils require preheating (e.g. to 40-50°C for a fuel oil to 200cS viscosity) prior to combustion. Often the fuel oil may be heated and cooled a number of times before combustion. This poses a problem since such heating generally causes water-in-oil emulsions to separate. The term "heat stable" as used herein means that the emulsion is stable to conditions of time and temperature to which the fuel oil itself is normally subjected prior to combustion. By the term "fuel oil" we mean fuel oil having a viscosity of 200-380cS and heavy fuel oils having nominal viscosities of 1000, 2000 and 6000 cS. Lighter fractions which do not require preheating, such as gasoline, automotive diesel fuel, gasoil, and industrial diesel fuel (light fuel oil of viscosity less than 200 cS), are excluded.

Claim

1. An emulsifier for producing heat stable (as herein defined) emulsions of water in a fuel oil (as herein defined), which comprises an admixture of
  - (i) 93-97 wt% of a sorbitan fatty acid monoester and
  - (ii) 3-7 wt% of polysorbate-80.

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3. An emulsion of water-in-fuel oil which is heat stable (as herein defined) and which comprises
- fuel oil (as herein defined),
  - 0.02-1% by volume of the emulsifier of either preceding claim based on the volume of the fuel oil, and
  - upto 25% by volume of water based on the volume of the fuel oil.



503404

Form 10

PATENTS ACT 1952

# COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number: PG 2696  
Lodged: 5 December 1983

This document contains the  
unpublished trade matter  
of the applicant.

Not to be used for printing.

Complete Specification—Lodged:  
Accepted:  
Lapsed:  
Published:

Priority:

Related Art:

36343/84

Name of Applicant:

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Sydney, N.S.W. 2000, Australia

LODGED AT SUB-OFFICE  
- 5 DEC 1984  
Sydney

Complete Specification for the invention entitled:

"EMULSIONS"

The following statement is a full description of this invention, including the best method of performing it known to me:—

Note: The description is to be typed in double spacing, pica type face, in an area not exceeding 250 mm in depth and 160 mm in width, on tough white paper of good quality and it is to be inserted inside this form.



The present invention relates to an emulsifier for producing heat-stable emulsions of water in fuel oil, and to the emulsions themselves. In particular the emulsions may be preheated prior to combustion.

5 It is well known that the addition of water to liquid hydrocarbon fuels so as to form an emulsion can have a number of beneficial effects as regards the combustion of the fuel. During combustion, the tiny droplets of water vaporise explosively within the fuel  
10 itself and lead to excellent atomisation of the fuel and improve combustion efficiency. Although the addition of the water detracts from the overall calorific value of the fuel, nevertheless small savings in overall fuel consumption can be achieved. Furthermore, the presence  
15 of the water tends to reduce the overall flame temperatures leading to lower nitrogen oxide emissions. The cleaner combustion also results in less emission of unburnt fuel components and carbon monoxide. Indeed, in the case of heavy fuel oils, the cleaner combustion of emulsified fuels may lead to substantial savings in  
20 furnace maintenance costs.

Hitherto, emulsified fuels have been burned in diesel engines by mechanically emulsifying the water with the oil shortly prior to combustion. Such emulsions are  
25 not stable over long periods and each engine must be fitted with its own emulsifier. Separate storage and handling systems must also be provided for the fuel and water respectively.

Stable emulsions of water in petroleum fractions  
30 obtained using an emulsifier are known from U.S. patent 3 876 391 and U.K. patent application 2 066 288. U.S. patent 3 876 391 discloses in Table 3 the use of an emulsifier blend of Tween-80 and Span-80 to produce emulsions of water in JP4 aviation fuel. U.K. patent  
35 application 2 066 288 discloses in Example 1 the use of sorbitan monooleate (a Span) and ethoxylated sorbitan monooleate (a Tween) to emulsify water in a mixture of

light fuel oil and methanol. However, these prior disclosures are concerned only with light petroleum fractions which do not require preheating to lower their viscosity prior to combustion.

5 Fuel oils require preheating (e.g. to 40-50°C for a fuel oil to 200cS viscosity) prior to combustion. Often the fuel oil may be heated and cooled a number of times before combustion. This poses a problem since such heating generally causes water-in-oil emulsions to separate. The  
10 term "heat stable" as used herein means that the emulsion is stable to conditions of time and temperature to which the fuel oil itself is normally subjected prior to combustion. By the term "fuel oil" we mean fuel oil having a viscosity of 200-380cS and heavy fuel oils having nominal viscosities  
15 of 1000, 2000 and 6000 cS. Lighter fractions which do not require preheating, such as gasoline, automotive diesel fuel, gasoil, and industrial diesel fuel (light fuel oil of viscosity less than 200 cS), are excluded.

It is an object of the present invention to provide an  
20 emulsifier capable of producing a heat stable emulsion of water in a fuel oil.

The present invention provides an emulsifier for producing heat-stable emulsions of water in a fuel oil, which comprises an admixture of

25 (i) 93-97 wt% of a sorbitan fatty acid monoester.  
and

(ii) 3-7 wt% of polysorbate-80.

Typically, the fatty acid is lauric, palmitic, stearic or oleic acid. The sorbitan monoester is preferably  
30 sorbitan monooleate (available under the trade name Span-80).

Polysorbate-80 is a widely used term for the oleate ester of sorbitol copolymerised with approximately 20 moles of ethylene oxide for each mole of sorbitol. The ratio of components (i) and (ii) is in the region 93-97:3-7% by  
35 weight. If too much component (ii) is used, the emulsion becomes too viscous. This advantageous ratio is not disclosed in the patent specification above.





The two components must be mixed together to provide the emulsifier before addition of water. Generally, the emulsifier is mixed with the water prior to addition of the hydrocarbon. Usually, emulsifier will be added in an amount of 0.02-1% by volume based on the hydrocarbon content. The water content may be up to 70% by volume of the hydrocarbon content. For normal use in an hydrocarbon fuel, the water content will usually be in the range 5-20%. However, where a particularly cool flame is required, for example in the flare stacks of drilling rigs, larger amounts of water e.g. up to 25% may be used.

The raw emulsion is then preferably passed through a centrifugal colloid mill in order to break up the water droplets.

In general, the water droplet size in the emulsion will be less than 100 microns. The drop size distribution generally varies dependent on the amount of water present. For example, in a typical 5% water emulsion, the majority of the water by volume was in drops between 10 and 25 microns in diameter, although a large number of much smaller drops were also present. For a 15% water emulsion, most of the water volume lay in drops in the region 50-100 microns.

The water-in-oil emulsion so produced is heat-stable over the long term and handles in a similar fashion to the hydrocarbon itself. In general, it is found that boiling and centrifuging do not substantially effect the emulsion.

Embodiments of the invention will now be described by way of example only with reference to the accompanying drawing and Examples.

#### Example 1 - Production of Water/Oil Emulsion

Figure 1 shows a continuous blending system wherein emulsifier (i.e. "additive") is introduced into a water flow in a predetermined amount. The mixture of water and emulsifier is then mixed with oil prior to passing into a

premixer tank equipped with a vane mixer. The premixed emulsion is then passed into a centrifugal colloid mill set at a 0.003 inch (0.008 cm) spacing so as to produce a water-in-oil emulsion.

5 The water, oil and additive flows are monitored as shown in the drawing and the data fed into a central controller, which in turn controls water flow valve 1, oil flow valve 2 and the dosing pump 3 via the dosing pump control. Ratio bias R allow the water/oil ratio to be set. Warning lights show if "no additive", "high additive" and "low oil" conditions occur. From the colloidal mill, the water-in-oil emulsion passes to a storage tank where it is usually preheated in a recirculating system before being combusted.

10 The emulsifier consisted of a mixture of 95% by volume sorbitan monooleate (Span 80 from Atlas Chemicals - a Trade Mark) and 5% by volume polysorbate-80 (Tween 80 - a Trade Mark).

15 The emulsifier content of the emulsion was 0.04 volume per cent based on the oil. For the purposes of the following tests, emulsions of 5%, 10% and 15% v/v water content were prepared. The oil was a heavy fuel oil.

20 For the 5% water emulsion, most of the water was in drops between 10 and 25 microns in diameter, with a large number (but small volume) of very small drops from 1-2 microns. For the 10% water emulsion, the very small drops were again observed, but the size range of drops was extended up to about 75 microns. For the 15% water emulsion, the very small drops were once again observed, with the larger drops extending in size up to about 100 microns and most of the water volume in drops from 50-100 microns.

25 The emulsions produced were opaque dark coffee-coloured liquids which were stable indefinitely.

#### 30 Example 2 - Combustion of Emulsions

Independent tests were carried out by the University of Newcastle, New South Wales into a comparison of the

combustion and heat transfer characteristics of heavy fuel oil with the water-oil emulsions as produced in Example 1.

5 A special experimental furnace was constructed which allowed measurement of fuel flow, flue gas composition, flue gas temperature, flame and radiation temperatures, heat absorption (by a water-cooled coil) and flame visualisation. This way it is possible to construct an overall heat balance.

10 Photograph of flames of neat oil, 5%, 10% and 15% v/v water in oil showed qualitatively that the water/oil emulsion fuels produced shorter, more intense flames with a higher peak flame temperature. This was confirmed by measurements of flame radiation with optical and total radiation pyrometers.

15 Measurements of the heat absorbed by the water-cooled coil surrounding the flame showed that the increased flame temperatures resulted in higher heat transfer rates and higher furnace thermal efficiencies. The greatest increase in efficiency was achieved with a 20 10% water in oil emulsion, and this also led to an increase in peak flame temperature of about 50°C.

25 The results of the heat balance on the furnace are given in the Table, which shows the percentage of heat absorbed in the water-cooled loop which is a measure of the heat produced in the flame. It can be seen that the amount of heat produced in the flame is generally greater for the water-in-oil emulsions, particularly for the 10% water content. However, it is generally noted that at 30 the lower water contents (e.g. 5%) there is a reduction in heat output, presumably due to the reduction in calorific value of the fuel exceeding the increase in combustion efficiency.

35



Table

		<u>Water Content % v/v</u>			
		0	5	10	15
	Thermal input %	100	100	100	100
5	Heat absorbed in				
	water-cooled loop %	38	35	44	41
	Flue gas loss %	43	42	44	44
	Wall loss %	10	11	10	10
	Unaccounted loss %	9	12	2	5

10 Example 3 - Comparison of Emulsion stabilities

A) Emulsions of water in heavy fuel oil were prepared using the following emulsifier blends falling outside the scope of the present invention

- i) sorbitan monooleate + Tween 20
- ii) sorbitan monooleate + Tween 81
- iii) dioctyl sodium sulfosuccinate + Tween 80
- iv) dioctyl sodium sulfosuccinate + Tween 81
- v) dioctyl sodium sulfosuccinate + Tween 20

In each blend the two components were varied from 5/95 wt% to 95/5 wt% in increments of 10 wt%.

In some cases stable water-in-oil emulsions resulted, but these emulsions separated once heated to 45°C. In no case did a heat-stable emulsion result.

B) Emulsions of water in heavy fuel oil were prepared using an emulsifier blend of sorbitan monooleate + Tween 80 in varying proportions from 5/95 wt% to 95/5 wt% in increments of 5 wt%. It was found that the following blend

95 wt% sorbitan monooleate + 5 wt% Tween 80 gave the best results in terms of producing a heat-stable water-in-oil emulsion.



CLAIMS

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An emulsifier for producing heat stable (as herein defined) emulsions of water in a fuel oil (as herein defined), which comprises an admixture of  
5 (i) 93-97 wt% of a sorbitan fatty acid monoester and  
(ii) 3-7 wt% of polysorbate-80.

2. An emulsifier according to claim 1, wherein the  
10 monoester is sorbitan monooleate.

3. An emulsion of water-in-fuel oil which is heat stable (as herein defined) and which comprises  
fuel oil (as herein defined).  
0.02-1% by volume of the emulsifier of either  
15 preceding claim based on the volume of the fuel oil, and  
upto 25% by volume of water based on the volume of the fuel oil.

20 4. An emulsion according to claim 3 wherein the water content is 5-20% by volume based on the volume of the fuel oil.

25 5. An emulsion according to claim 3 or 4 wherein substantially all the water droplets have a size less than 75 microns.

30 DATED this 18th day of May, 1987

HYDROLINE AUSTRALIA PTY. LIMITED

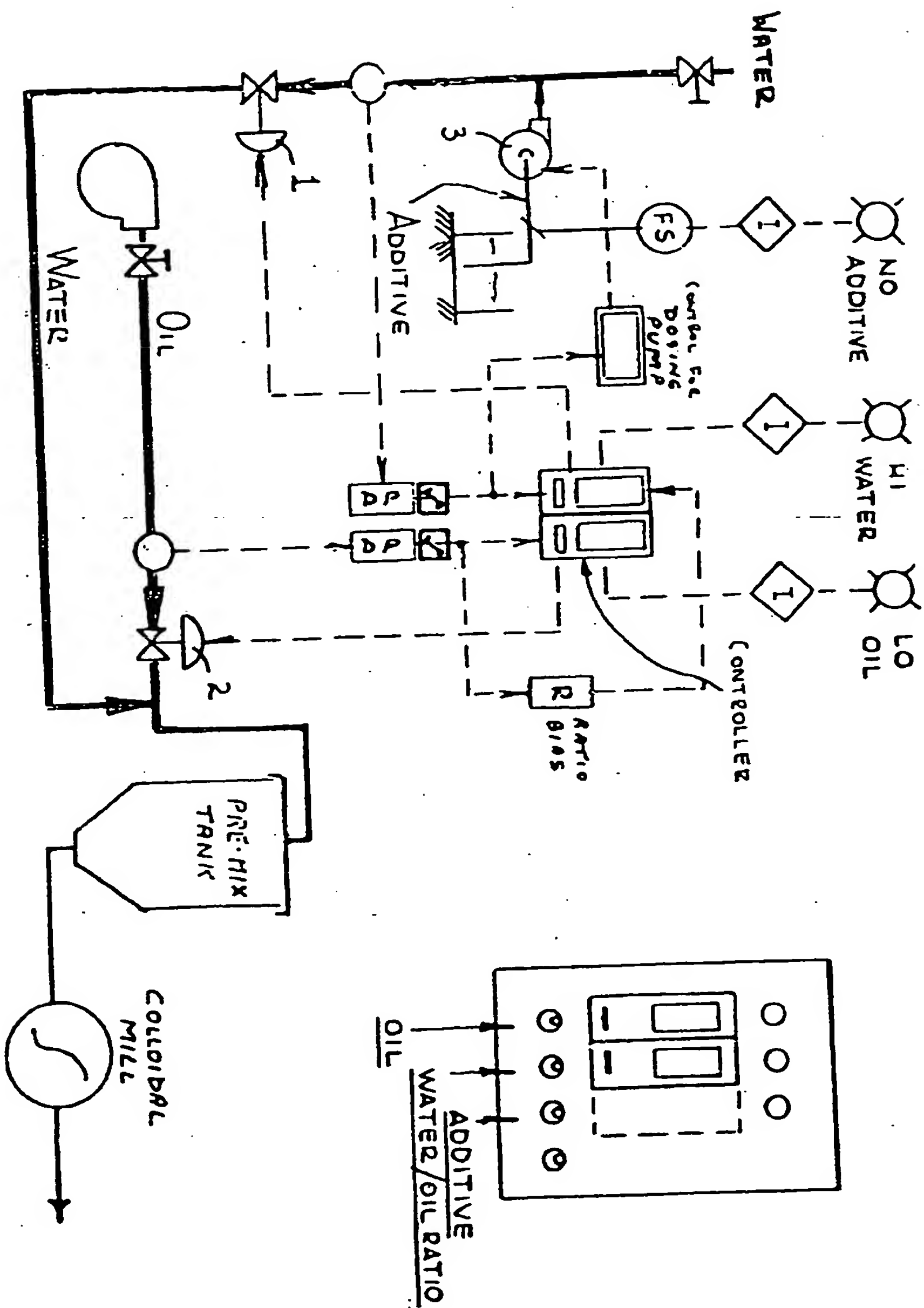
By their Patent Attorneys

35 GRIFFITH HASSEL & PRAZER

4863S/MS



DRAWINGS

$$36343 / 84$$


4.6.11

A 4x4 grid of dots forming the number 1010. The first column has dots in rows 1, 2, 3, and 4. The second column has dots in rows 1, 2, 3, and 4. The third column has dots in rows 1, 2, 3, and 4. The fourth column has dots in rows 1, 2, 3, and 4.



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